Does the recent IUPAC definition on hydrogen bonding lead to new intermolecular interactions?

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Hydrogen bonding interaction is one of the most important intermolecular interactions. This interaction has been known almost for a century[1], but it is popular only after the work of Pauling[2], who was the first to give a definition of the hydrogen bond. According to Pauling, 'under certain conditions an atom of hydrogen is attracted by rather strong forces to two atoms, instead of only one, so that it may be considered to be acting as a bond between them. This is called the hydrogen bond'. This interaction may be designated as X–H•••Y. X–H is the hydrogen bond donor in which X and H are covalently bound and Y is the acceptor. Pauling[3] considered both X and Y to be electronegative atoms mainly O, N, F. There are many systems which would not be considered as hydrogen bonds according to Pauling's definition. One example is the C–H•••O interaction. This is now accepted as weak hydrogen bond, as the interaction plays an important role in many systems[4,5]. After the work of Pauling, numerous experimental and theoretical studies on these interactions have been made, from which it is now well established that X can be any atom or a fragment whose overall electronegativity is more than that of hydrogen and Y can be any electron-rich region in a molecule, such as a lone pair, π pair, unpaired and σ electrons. A recent report has recognized the diverse nature of hydrogen bond donors and acceptors[6]. The study of hydrogen bonding is of special interest for a variety of reasons. It is one of the most common interactions and is found in many systems. The relatively high boiling point of water is a classic example of hydrogen bonds. Hydrogen bonding interaction is found in biological systems. It plays a role in determining the shapes of folded proteins and in linking base pairs in strands of DNA[5,7].

According to the new IUPAC definition[8], the hydrogen bond is an attractive interaction between a hydrogen atom from a molecule or a molecular fragment X–H in which X is more electronegative than H, and an atom or a group of atoms in the same or a different molecule, in which there is evidence of bond formation. From this definition, this interaction may be designated as X–H•••Y–Z. With following criteria given in the IUPAC report[8] this interaction it is now believed to be fully understood.

(a) The forces involved in the formation of a hydrogen bond include those of an electrostatic origin, those arising from charge transfer between the donor and acceptor leading to partial covalent bond formation between H and Y, and those originating from dispersion.

(b) The atoms X and H are covalently bonded to one another and the X–H bond is polarized, the H–Y bond strength increasing with the increase in electronegativity of X.

(c) The X–H—Y angle is usually linear (180°), and closer the angle is to 180°, stronger is the hydrogen bond and shorter is the HY distance.

(d) The length of the X–H bond usually increases on hydrogen bond formation leading to a red shift in the infrared X–H stretching frequency and an increase in the infrared absorption cross-section for the X–H stretching vibration. The greater the lengthening of the X–H bond in X–H—Y, the stronger is the HY bond. Simultaneously, new vibrational modes associated with the formation of the HY bond are generated.

(e) The X–H—Y–Z hydrogen bond leads to characteristic NMR signatures that typically include pronounced proton deshielding for H in X–H, through hydrogen bond spin–spin couplings between X and Y, and nuclear Overhauser enhancements.

(f) The Gibbs energy of formation for the hydrogen bond should be greater than the thermal energy of the system for the hydrogen bond to be detected experimentally[8].

After the recent definition of hydrogen bonding given by IUPAC, many researchers around the world have studied and characterized different types of intermolecular interactions. According to a *Google Scholar* search on 18 September 2015, 387 researchers had cited the recent definition of hydrogen bond given by IUPAC till that day. We found that these records were journal articles, thesis and scientific papers in different languages. When same was searched in *Web of Science* (*WoS*) on the same date and around the same time, the number of citations recorded was 274. However, in the *WoS* records we found that only journal articles published in English cited this recent definition. Moreover, the works related with various types of intermolecular interactions also cited this new IUPAC definition of hydrogen bonding. These different of intermolecular interactions are discussed briefly here.

Halogen bond

With the progress in the study of hydrogen bonding, different intermolecular interactions have been predicted. Among these, the halogen bond is a conceptually similar phenomenon and was reported earlier than hydrogen bond[9]. But it has received attention only after the work by Hassel nearly a century later[10]. σ-Hole concept is applied to understand this interaction (σ-hole is a region of positive electrostatic potential that is present in the outermost portions of R−X of R−X•••Y−Z interaction). An understanding of the halogen bonding interactions that exist between molecules has applications in many fields such as molecular recognition[11], crystal engineering[12] and biological systems[13]. Because of its importance in many fields, IUPAC has recently defined halogen bond as follows[14]: 'a halogen bond, R−X•••Y−Z, occurs when there is evidence of a net attractive interaction between an electrophilic region on a halogen atom X belonging to a molecule or a molecular fragment R−X (where R can be another atom, including X, or a group of atoms) and a nucleophilic region of a molecule, or molecular fragment, Y−Z'.

Lithium bond

Hydrogen bonding and halogen bonding are well-known. There have been several reports of analogous lithium bonding. The existence of lithium bonding was

predicted theoretically by Kollman *et al.*[15]. Experimental identification was made by Ault and Pimentel[16]. Like hydrogen bonding and halogen bonding, lithium bonding has been studied thoroughly, such as blue shifting lithium bonding[17], single-electron lithium bonding, σ and π electrons lithium bonding, etc.[18]. However, more recently, it is found that lithium bonding is more ionic than hydrogen/halogen bonding[19].

Chalcogen bond

Chalcogen bonding is the non-covalent interaction between an electron-deficient, covalently bonded chalcogen (group 16 elements of the periodic table) and electron donor atoms (Y) which may be designated as Chal•••Y. A number of research groups have investigated this bonding. The first report[20] of chalcogen bonding was published in 1977 followed by a similar type of non-covalent interaction four years after the first one[21]. Most of the earlier studies of this interaction were in solid state[22–25]. This bond was fully studied using *ab intio* method only in 2006 (ref. 26). Literature search shows that many publications of this interaction have been made after the recent IUPAC definition on hydrogen bonding. Furthermore, to know more about this interaction comparative studies with other intermolecular interactions have been performed[27]. Additionally, it is found that these interactions can occur in a variety of situations, including chalcogen bonding in solutions[28], chalcogen bonds with π electrons[29], etc.

Like hydrogen and halogen bonds these interactions have been found to have relevance in crystallization of pharmaceuticals[23], solid-state ordering of materials[30], organic reactivity[24] and folding of biomolecules[25].

Pnicogen bond

Interaction of group 15 elements of the periodic table falls under this type of bonding. There have not been many studies of this interaction before the recent IUPAC definition on hydrogen bonding[31]. Schiener *et al.*[32] and Zahn *et al.*[33] reported simultaneously this interaction in 2011. At that time the remarkable work by Arunan *et al.*[6,8], the IUPAC new definition of hydrogen bonding was about to publish. More research teams around the world started investigating this interaction and now this bonding is as popular as other intermolecular interactions. In hydrogen bonding, halogen bonding and lithium bonding there is an intermediate atom (for example, in H-bonding, X–H•••Y, there is a H atom). But in this bond there is no intermediate atom. Furthermore, in pnicogen bond a σ-hole is not necessary, despite the similarities between halogen bonding and pnicogen bonding[34]. There have been many investigations on this type of bonding after the recent IUPAC definition on hydrogen bonding. Some of them are: direct N–N pnicogen bond[35], cationic pnicogen complexes[36], the strength of pnicogen bond (involving N, P, and As)[37], and substituent effects on cooperativity of pnicogen bonds[38]. The participation of nitrogen atom in this bonding has been experimentally verified recently[39].

Carbon bonding/tetral bonding

The interaction of group 14 elements of the periodic table is called tetral bonding. The existence of this type of interaction was known earlier[40,41] and was analysed in detail mainly for silicon and germanium; carbon is included in one of the reports[42]. Carbon bond is considered as a sub-class of tetral bond and the nature of this bonding was known only after the work of Mani and Arunan[43]. While studying Ar•••propargyl alcohol dimer, the evidence regarding carbon bonding was found. In this work[42], not only the expected OH•••Ar and π•••Ar interactions were found, but also C•••Ar interaction. With this insight, Mani and Arunan[43] extended their study on complexes of methanol and methyl fluoride with H_2O, H_2S, NH_3, PH_3, HF, HCl, HBr, ClF, LiF, LiCl and LiBr molecules. The results of this work were found to be similar to hydrogen bonding interaction. Thus, this was designated as X–C•••Y type interaction and named carbon bonding, where X is the carbon bond donor and Y the carbon bond acceptor. On the basis of charge density analysis, experimental evidence supporting carbon bonding in solid state was found[44]. Like other intermolecular interactions, tetral bond with π electrons[45] and single electrons[46], tetral-hydride[47] interactions have recently been investigated.

Moreover, the tetral/carbon bond is also important like other intermolecular interactions. For examples, this bond could play an important role in hydrophobic interactions and in the stabilization of intermediates to the S_N2 reaction[43,48].

Sodium bond

Sodium bond was first studied by Kulkarni and Rao[49]. There was not much works done on this bonding, nor experimental verification. After a long gap, this bonding has been studied addressing various acceptors such as unpaired and π electrons[50]. After the recent IUPAC definition of hydrogen bonding, a comprehensive and systematic investigation of Na-bonding was taken up by comparing their properties with analogous hydrogen and lithium-bonded complexes. This recent work showed that sodium bonding is the same as ionic bonding and this bonding could exist only for certain acceptors[51].

Triel bond

This is a recently identified interaction of group 13 elements of periodic table[52]. This interaction is understood from π-hole concept (π-hole is a region of positive electrostatic potential perpendicular to the centre of a planar molecule or a planar portion of a molecular framework).

Beryllium bond

The interaction of beryllium atom was identified after the recent IUPAC definition on hydrogen bonding while studying BeX_2(X=H, F) with water molecules and was named beryllium bonding interaction[53]. Cooperativity in beryllium bonds[54] and π-beryllium bonds have recently been analysed[55].

Aerogen bond

In aerogen bonding interaction, noble gases (group 18 of the periodic table) elements involve. The evidence of this type of interaction was recently found between a covalently bonded aerogen atom and lone pair of a Lewis base or an anion. It has been reported in this study

that this interaction is due to σ-hole region[56]. More recently, a study of π-hole aerogen bonding interactions was reported by the same group[57].

New types of hydrogen bonds

In recent years, new types of hydrogen bonds have been predicted and analysed. These include anti-electrostatic hydrogen bonding, homopolar dihydrogen bonding and sulphur centre hydrogen bonding.

Unlike most of other hydrogen bonding interactions, ions of like charge (anion–anion and cation–cation) are involved in anti-electrostatic hydrogen bonding interactions. The existence of this type of interaction has been detected in various complexes. Some of the examples are between fluoride (F^-) and bicarbonate (HCO_3^-) anions as well as the hydronium complex (H_2OH^+) and protonated aminomethanol ($OHCH_2NH_3^+$), etc.[58].

Homopolar dihydrogen bond (X–H●●●H–X) is the interaction between two similar moieties. Although heteropolar dihydrogen interaction (X–H●●●H–Y) was observed in the late 1960s (ref. 59), it was analysed only in 2003. This reported interaction between two C–H moieties in phenanthrene (**1**), chrysene, etc.[60]. Furthermore, it is found that there is more contribution of van der Waals forces than electrostatic forces for this interaction[61].

Hydrogen bonding interaction can occur with a variety of acceptors and donors. Hydrogen bonding involving S is another class of interactions in which S can act either as a donor/acceptor or it can act as both donor and acceptor. Hydrogen sulphide dimer (H_2S–H_2S) is the simplest model system of this type of interaction[62]. The electronegativity of sulphur atom is less than that of oxygen and nitrogen, so sulphur involving hydrogen bonding interactions should be weaker than other conventional hydrogen bonding interactions. However, amide–N–H●●●S hydrogen bonds in methionine containing dipeptides are stronger than amide–N–H●●●O=C hydrogen bonds[63].

Conclusion

With the advancement of various theoretical as well as experimental techniques that have been applied to various systems over the years, different types of intermolecular interactions have been predicted and analysed. Literature search shows that some of them were predicted after the recent IUPAC definition on hydrogen bonding.

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